

CLAIMS

1. A process for the preparation of ethylene polymers, comprising the polymerization reaction of ethylene and optionally one or more olefins, in the presence of a catalyst comprising the product obtainable by contacting:

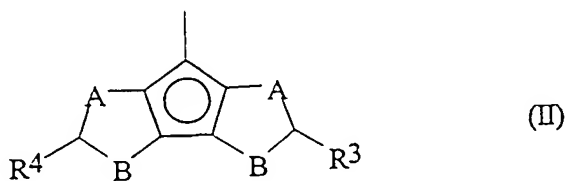
A) a metallocene compound of the general formula (I):



wherein SiR^1R^2 is a divalent group bridging the moieties L and Q;

R^1 and R^2 , which may be the same or different, are selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl or $\text{C}_7\text{-C}_{20}$ -arylalkyl radical optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; optionally R^1 and R^2 form a ring comprising from 3 to 8 atoms, which can bear substituents;

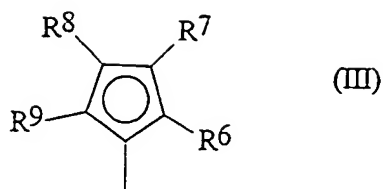
Q is a moiety of formula (II):



wherein A and B are selected from sulfur (S), oxygen (O) and CR^5 , R^5 is selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl or $\text{C}_7\text{-C}_{20}$ -arylalkyl radicals optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; either A or B being different from CR^5 , and wherein the rings containing A and B have a double bond in the allowed position having an aromatic character; if A is S or O, B is CR^5 or if B is S or O, A is CR^5

R^3 and R^4 , which may be the same or different, are selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl or $\text{C}_7\text{-C}_{20}$ -arylalkyl optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

L is a moiety of formula (III):



wherein R^6 , R^7 , R^8 and R^9 , which may be the same or different, are selected from C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; and two adjacent R^6 and R^7 and/or R^8 and R^9 can form a ring comprising from 3 to 8 atoms, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; and can bear substituents;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version),

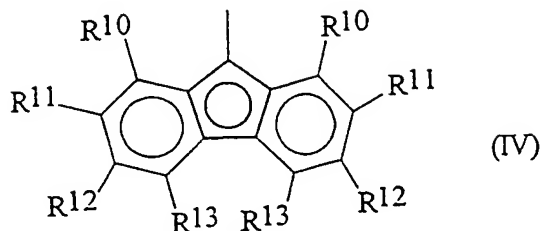
X, which may be the same or different, is a ligand selected from hydrogen, halogen, R^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10}_2 or PR^{10}_2 group, wherein R^{10} is selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

p is an integer of from 1 to 3, being equal to the oxidation state of the metal M minus 2; and

(B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

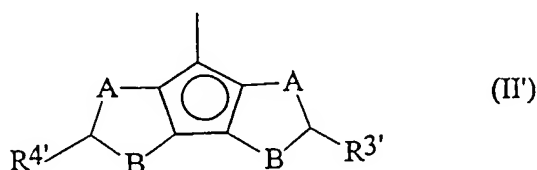
2. The process according to claim 1, wherein in the metallocene compound of formula (I) the transition metal M is selected from titanium, zirconium and hafnium.
3. The process according to any of claims 1 to 2, wherein in the metallocene compound of formula (I) the X substituents are chloride or methyl radicals.
4. The process according to any of claims 1 to 4 wherein A is sulfur and B is a CH radical.
5. The process according to any of claims 1 to 3, wherein in the metallocene compound of formula (I): R^1 and R^2 are C_1 - C_{20} -alkyl groups such as methyl group; R^3 and R^4 are C_1 - C_{20} -alkyl groups optionally containing silicon atoms or C_6 - C_{20} -aryl groups; R^6 , R^7 , R^8 and R^9 are C_1 - C_{20} -alkyl groups.
6. The process according to any of claims 1 to 4, wherein in the metallocene compound of

formula (I) L is a moiety of formula (IV):



wherein R^{10} , R^{11} , R^{12} and R^{13} , which may be the same or different, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and optionally two adjacent R^{10} , R^{11} , R^{12} and R^{13} groups can form a ring having 3 to 8 atoms, which can bear substituents.

7. The process according to claim 6, wherein R^{10} , R^{12} and R^{13} are hydrogen and R^{11} are selected from hydrogen and a C_1 - C_{20} -alkyl group.
8. The process according to claim 7, wherein R^{11} is selected from hydrogen and a tert-butyl radical.
9. The process according to any of claims 1 to 4, wherein in the metallocene compound of formula (I) L is a moiety of formula (II'):

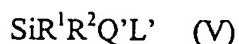


wherein A and B are defined as in claim 1, $R^{3'}$ and $R^{4'}$, which may be the same or different, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements.

10. The process according to claim 9 wherein A is sulfur and B is a CH radical, $R^{3'}$ is the same as $R^{4'}$, and they are selected from a C_1 - C_{20} -alkyl group.
11. The process according to any of claims 1 to 10, wherein said alumoxane is obtained by contacting water with an organo-aluminium compound of formula $H_jAlR^{15}_{3-j}$ or $H_jAl_2R^{15}_{6-j}$, where R^{15} substituents, which may be the same or different, are hydrogen atoms, C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl,

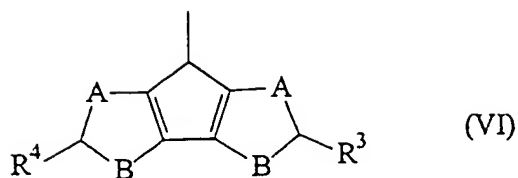
optionally containing silicon or germanium atoms with the proviso that at least one R^{15} is different from halogen, and J ranges from 0 to 1, being also a non-integer number.

12. The process according to claim 11, wherein the molar ratio between the aluminium and water is in the range of 1:1 and 100:1.
13. The process according to any claims 1 to 10, wherein said alumoxane is MAO, TIBAO and TIOAO, and said organo-aluminium compound is TIOA, TMA and/or TIBA.
14. The process according to any of claims 1 to 10, wherein the compound capable of forming a metallocene alkyl cation is a compound of formula D^+E^- , wherein D^+ is a Brønsted acid, able to give a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E^- is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be removed by an olefinic monomer.
15. The process according to claim 14, wherein the anion Z^- comprises one or more boron atoms.
16. The process according to any of claims 1 to 15, wherein the process is carried out in the presence of an alpha-olefin selected from propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and 1-dodecene.
17. The process according to claim 16, wherein said alpha-olefin is selected from 1-hexene, propylene and 1-octene.
18. The process according to any of claims 16 to 17, wherein the molar content of alpha-olefin derived units is comprised between 0% and 60%.
19. The process according to any of claims 1 to 18, wherein the process is carried out in the presence of a cyclic comonomer.
20. The process according to claim 19, wherein said cyclic comonomer is 5-ethylidene-2-norbornene.
21. The process according to any of claims 19 to 20, wherein the molar content of the cyclic comonomer is comprised between 0mol% and 30mol%.
22. The process according to any of claims 1 to 21 being carried out in the gas phase.
23. A process for the preparation of a ligand of formula (V):



wherein

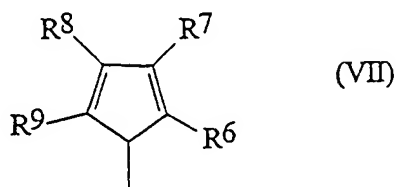
Q' is a moiety of the general formula (VI):



and its double bond isomers,

wherein A, B, R³ and R⁴ are defined as described as in claim 1;

L' is a moiety of the general formula (VII):

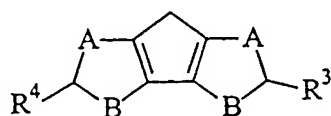


and its double bond isomers,

wherein R¹, R², R⁶, R⁷, R⁸ and R⁹ are defined as described as in claim 1,

comprising the following steps:

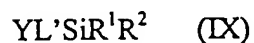
- iii) treating the compound of formula (VIII) with at least one equivalent of a base selected from the group consisting of metallic sodium and potassium, sodium and potassium hydroxide and an organolithium compound;



(VIII)

wherein the rings containing A and B have a double bond in the allowed position having an aromatic character, A, B, R³ and R⁴ are defined as above;

- iv) contacting the corresponding anionic compound obtained under i) with a compound of general formula (IX):

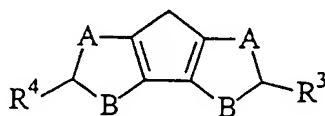


wherein L', R¹, R² have the meaning described as in claim 1 and Y is a halogen atom selected from the group consisting of fluoride, chloride, bromide and iodide;

- 24 A process for the preparation of a ligand of formula (V) as defined in claim 23 comprising the following steps:

- i) treating the compound of formula (VIII) with at least one equivalent of a base

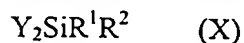
selected from the group consisting of metallic sodium and potassium, sodium and potassium hydroxide and an organolithium compound;



(VIII)

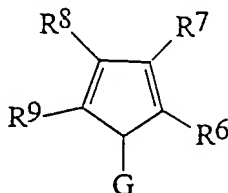
wherein the rings containing A and B have a double bond in the allowed position having an aromatic character; A, B, R³ and R⁴ are defined as in claim 1;

- ii) contacting the corresponding anionic compound obtained under i) with a compound of general formula (X):



wherein L', R¹, R² have the meaning described in claim 1 and Y is a halogen atom selected from the group consisting of fluoride, chloride, bromide and iodide;

- iii) contacting the product obtained in step ii) with a compound of formula (XI)



(XI)

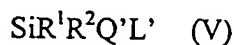
wherein R⁶, R⁷, R⁸ and R⁹ are described as in claim 1 and G is selected from sodium, potassium and lithium,

25. A process for the preparation of a metallocene of the general formula (I):



wherein Q, L, R¹, R², M, X and p have the meaning as defined in claim 1, comprising the following steps:

- a) contacting a ligand of formula (V):



wherein

Q', L', R¹ and R² are defined as in claim 26 with a base, wherein the ratio between said base and the compound of formula (V) is at least 2,

- b) contacting the obtained product with a compound of formula MX_{p+2}, wherein M,

X and p are defined as in claim 1.

26. A copolymer of ethylene with propylene and a polyene, having a content of ethylene derived units comprised between about 35mol% and 85mol%, a content of C₄-C₁₀-alpha-olefin derived units comprised between about 10mol% and 60mol% and a content of a C₄-C₃₀-polyene derived units comprised between about 0.1mol% and 5mol%, and having the following characteristics:
- (A) the % by mole content of the α -olefin in the copolymer (% α) and the ratio $E\alpha E/(E\alpha E + \alpha\alpha E + \alpha\alpha\alpha)$, wherein E α E, $\alpha\alpha$ E and $\alpha\alpha\alpha$ represent the sequences ethylene/ α -olefin/ethylene, α -olefin/ α -olefin/ethylene and α -olefin/ α -olefin/ α -olefin respectively in the copolymer, satisfy the following relationship:
- $$0.01\% \alpha + E\alpha E/(E\alpha E + \alpha\alpha E + \alpha\alpha\alpha) \geq 1$$
- (B) less than 2% of the CH₂ groups in the polymeric chain are sequences (CH₂)_n, wherein n is an even number.
27. A copolymer according to claim 26, in which the product of the reactivity ratios $r_1 \cdot r_2$, wherein r_1 is the reactivity ratio of the α -olefin and r_2 that of ethylene, is lower than 0.2.
28. A copolymer according to any of claims 26 to 27, having an intrinsic viscosity (η) > 0.5.
29. A copolymer according to any of claims 26 to 28, further containing a polyene.
30. A metallocene compound of formula (I)
- $$\text{SiR}^1\text{R}^2\text{LQMXp} \quad (\text{I})$$
- wherein R¹, R², L, Q, M, X and p have the meaning as in claims 1-10.
31. A ligand of formula (V):
- $$\text{SiR}^1\text{R}^2\text{Q'L'} \quad (\text{V})$$
- wherein R¹, R², L' and Q' have the meaning as in claims 1-10.
32. A process according to claim 22 wherein the olefin polymerization catalyst system impregnate a polymer previously prepared, provided that said polymer is from 10 to 70% of the total polymer obtained in the process.